

# PATENT ABSTRACTS OF JAPAN

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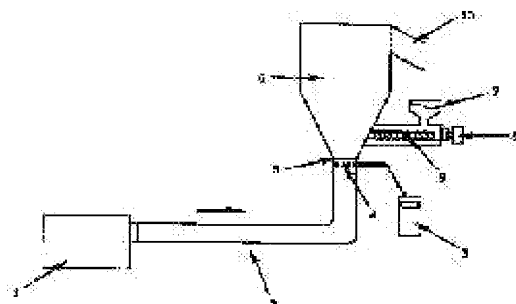
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## (54) METHOD AND APPARATUS FOR EXPANDING EXPANDABLE VINYLIDENE CHLORIDE RESIN PARTICLE

### (57)Abstract:

**PURPOSE:** To obtain high-expansion-ratio expanded particles having a stable cellular structure within short time by a simple apparatus by expanding specified expandable resin particles with hot air from an electrical hot air generator under specified conditions.

**CONSTITUTION:** Expandable particles of a vinylidene chloride resin having a partially crosslinked structure (e.g. particles prepared by impregnating resin particles made from vinylidene chloride, styrene, acrylonitrile, N-phenylmaleimide and 1,6-hexanediol diacrylate with a monochlorodifluoroethane blowing agent) are expanded with hot air from an electrical hot air generator under conditions in which the temperature of the hot air in the expansion tank 6 is 100–300° C, and the residence time is 0.1–60min. In a desirable example, the apparatus for expansion consists of a hot air generator 1, a heat-resistant hose 2 for supplying hot air and an expansion tank 6 having a feed supply part 7 and expanded particle discharge part 10.



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## CLAIMS

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[Claim(s)]

[Claim 1] The foaming approach characterized by becoming the multi-foam quality structure  
where are the approach of foaming to the vinylidene-chloride system resin fizz particle which  
has the partial structure of cross linkage by the hot blast by the electric-type hot blast  
generating machine, and the foaming particle which the temperature of the hot blast in a foaming  
tub foams below 100 degrees C or more 300 degrees C, and the residence time makes foam in  
60 or less minutes 0.1 minutes or more was stabilized.

[Claim 2] Equipment to which the vinylidene-chloride system resin fizz particle which consists of  
foaming tubs with the hot blast generating machine which generates 100-degree-C or more hot  
blast 300 degrees C or less, the heat-resistant hose which supplies this hot blast, the feeding  
section, and the foaming particle discharge section is made to foam.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the method of being spots, such as a civil work,  
and manufacturing a foaming particle easily that the foaming particle of the high expansion ratio  
in a short time is needed by still more detailed simple equipment, and its equipment, about the  
foaming approach of the fizz vinylidene-chloride system resin particle which makes hot blast by  
the electric-type hot blast generating machine the source of heating.

[0002]

[Description of the Prior Art] Conventionally, as the foaming approach of the fizz resin particle in  
the spot for which a foaming particle is needed, the approach of making a steam the source of

heating by the polystyrene system resin particle is learned as indicated by JP,35-11780,B and JP,38-16776,B. However, since polystyrene system resin be lacking in gas barrier nature, if heating time in a steam or hot blast be lengthen too much, by the vaporization to the particle exterior of a foaming agent, contraction of a foaming particle take place, the phenomenon in which expansion ratio fall conversely arise, and control of expansion ratio be difficult for expandable polystyrene system resin as indicate by Chapter 2 of a form handbook ( the Nikkan Kogyo Shimbun issue, February 28, Showa 48 first edition).

[0003] In order not to reduce the expansion ratio of polystyrene system resin and to carry out a permutation with the air of foaming gas in fact, in foaming in place, equipment becomes large-scale and actuation also becomes complicated. Moreover, as long as a steam is made into the source of heating, steamy generating etc. needs to be furnished, therefore equipment is enlarged, and a heavy-duty truck etc. is needed for equipment carrying in at the spot for which a foaming particle is needed, for example, it is not put in practical use in a civil work site.

[0004]

[Problem(s) to be Solved by the Invention] The purposes of this invention are spots, such as a civil work for which a foaming particle is needed by the simple equipment which makes hot blast by the electric-type hot blast generating machine the source of heating, and are offering the manufacture approach and a manufacturing installation effective in the manufacture approach for the foaming particle of the high expansion ratio in a short time.

[0005]

[Means for Solving the Problem] This invention is the approach of foaming to the vinylidene-chloride system resin fizz particle which has the partial structure of cross linkage by the hot blast by the electric-type hot blast generating machine, and is the foaming approach characterized by becoming the multi-foam quality structure where the foaming particle which the temperature of the hot blast in a foaming tub foams below 100 degrees C or more 300 degrees C, and the residence time makes foam in 60 or less minutes 0.1 minutes or more was stabilized.

[0006] Moreover, this invention is equipment to which the vinylidene-chloride system resin fizz particle which consists of foaming tubs with the hot blast generating machine which generates 100-degree-C or more hot blast 300 degrees C or less, the heat-resistant hose which supplies this hot blast, the feeding section, and the foaming particle discharge section is made to foam. This invention can be attained by using the vinylidene-chloride system resin fizz particle which serves as multi-foam quality structure which the foaming particle stabilized as a fizz resin particle.

[0007] Vinylidene-chloride system resin is resin excellent in gas barrier nature. Therefore, there is that the foaming agent inside a particle vaporizes [ little ] at the time of foaming, and since there is nothing that is seen when an expandable polystyrene system resin particle is used as a fizz resin particle and in which a foaming agent vaporizes rapidly like, even if it protracts heating time, contraction of a foaming particle is made into the multi-foam quality structure which stabilized the foaming particle without happening, and can carry out things. For this reason, it is easy equipment which makes hot blast by the electric-type hot blast generating machine the source of heating, and it is the spot of the engineering-works site for which a foaming particle is needed, and it is possible to manufacture the foaming particle of the high expansion ratio in a short time.

[0008] An electric-type hot blast generating machine is comparatively easy to adjust the temperature of hot blast, and airflow, and as for vinylidene-chloride system resin, there is that the foaming agent inside a particle vaporizes [ little ] at the time of foaming, and its adjustment of foaming also with simple equipment is easy also for saying to it. The fizz vinylidene-chloride system resin particle used for this invention is indicated by JP,63-122745,A, JP,63-122713,A, JP,04-085343,A, etc.

[0009] That is, a foaming agent is sunk into the whole resin layer at homogeneity at the amorphous vinylidene-chloride system resin particle which carried out partial bridge formation. An amorphous vinylidene-chloride system resin particle can be obtained by copolymerizing 10 % of the weight or more and 85% of the weight or less of a vinylidene chloride with 15 % of the weight or more and 90% of the weight or less of vinylidene chlorides [ one or more kinds of ], and

a copolymerizable monomer. Gas barrier nature falls that the content of a vinylidene chloride is less than 10 % of the weight, and vaporization of the foaming agent at the time of foaming cannot be prevented. On the other hand, if it exceeds 85 % of the weight, resin will serve as crystallinity and sinking [ of a foaming agent ] in will become difficult.

[0010] As a vinylidene chloride and a copolymerizable monomer, N-permutation maleimide, such as acrylic ester (meta), such as AKURIRONIRO (meta) nitril, styrene and its derivative, and a methyl acrylate (meta), and N-phenyl maleimide, can be mentioned. Furthermore, the stability of multi-foam quality structure increases by carrying out partial bridge formation. What is necessary is just to carry out suitable amount copolymerization of the monomer which has two copolymeric double bonds, such as a divinylbenzene and methacrylic acid ester of aliphatic series polyhydric alcohol, in intramolecular, in order to introduce partial bridge formation.

[0011] Although well-known polymerization methods, such as a suspension-polymerization method, an emulsion-polymerization method, and a solution polymerization method, can be used for the polymerization method of this vinylidene-chloride system resin particle, its suspension-polymerization method for the ability to obtain a polymer by the shape of a particle is desirable. As particle diameter, it is desirable that it is [ 0.1mm or more ] 5.0mm or less. In less than 0.1mm, if the fluidity of a particle worsens and it exceeds 5.0mm preferably on handling, the impregnating ability of a foaming agent will fall.

[0012] In order to attain the purpose of this invention, it is required for a fizz vinylidene-chloride-resin particle to serve as multi-foam quality structure stabilized at the time of foaming. In order to consider as multi-foam quality structure, it is required to sink a foaming agent into the whole resin layer at homogeneity. Since it becomes single air bubbles at the time of foaming, it becomes easy to contract, and a foaming agent cannot be made to foam only under a certain certain narrow conditions in endocyst and the encapsulated thing. Foaming under broad conditions is attained for the first time by becoming multi-foam quality structure. the same — even if it is a fizz vinylidene-chloride system resin particle, thermoplastics, such as vinylidene-chloride-acrylonitrile, is used as an outer core, and since a foaming particle serves as single air bubbles at the time of foaming, endocyst and the encapsulated fizz particle (for example, the trade name of EXPANCEL, the product made from Japanese FIRAITO, Inc.) can foam to a foaming agent only under certain conditions.

[0013] As an approach for sinking a foaming agent into homogeneity at the whole resin layer, the underwater suspension method which adds a foaming agent for this resin particle and a foaming agent to the water slurry of the shape of a gas, the direct sinking-in method it is liquid and make it contact directly, and a resin particle, the polymerization sinking-in method make the foaming agent live together at the time of a polymerization, etc. can be used for a vinylidene-chloride system resin particle. In order for a foaming agent to check sinking into the whole resin layer at homogeneity, distribution of the foaming agent in a resin particle can be investigated by the infrared spectrophotometer, an elemental-analysis method, etc.

[0014] As a foaming agent, HFC, such as HCFCs;1 [ , such as halogenated hydrocarbon; monochlorodifluoroethane (HCFC142b), ], such as hydrocarbons; methyl chlorides, such as a propane, butane, a pentane, and a cyclopentane, and an ethyl chloride, 1 and 1, and 2-tetrafluoro ethane (HFC134a), can be used, for example. In this invention, 100 degrees C or more 300 degrees C or less of hot blast temperature are desirable. When hot blast temperature is less than 100 degrees C, expansion ratio is not enough, and when exceeding 300 degrees C, a foaming resin particle pyrolyzes.

[0015] Moreover, in this invention, the residence time of the resin particle exposed to hot blast has 60 or less desirable minutes 0.1 minutes or more. When the residence time is less than 0.1 minutes, expansion ratio is not enough, and when exceeding 60 minutes, a foaming particle pyrolyzes. The pre-expansion vinylidene-chloride system resin particle which the non-foamed vinylidene-chloride system resin particle could be made to foam directly, and was made to foam beforehand may be made to foam further in this invention.

[0016] Drawing 1 is a mimetic diagram which illustrates simple foaming equipment effective in achievement of the manufacture approach of this invention. The electric-type hot blast generating machine (1) is marketed by the trade name (Made in the Taketsuna Factory) of for

example, a TSK-10 mold hot blast generating machine. The generated hot blast lets a heat-resistant hose (2) pass, and is ventilated by the foaming tub (6). The temperature controller of a hot blast generating machine is adjusted so that the hot blast temperature ventilated in a foaming tub may be measured and hot blast temperature may turn into predetermined temperature with a thermometric element (3). A fizz vinylidene-chloride system resin particle is supplied in a foaming tub with through and a screw (9), and the raw material hopper of (7) is made to foam by hot blast. The foaming particle which became small [ specific gravity ] is discharged by hot blast from an exhaust port (10). The hot blast rate in the foaming tub upper part performs adjustment of the expansion ratio of the foaming particle discharged. That is, if a hot blast rate is gathered, expansion ratio will become small, and expansion ratio will become large if a hot blast rate is lowered.

[0017] Since it may ignite when a foaming agent is inflammable gas, it is required to operate it out of the explosion limit by taking the measure in which the hot blast in a foaming tub prevents a back flow to a hot blast generating machine, or adjusting the blast weight and the discharge of hot blast. Since the point vinylidene-chloride system resin is excellent in gas barrier nature, the range which chooses the outside of the explosion limit is wide. Moreover, in order to prevent the welding of the particles within a hot blast tub, inorganic, organic fine particles, etc. can be made to be placed between particle front faces.

[0018]

[Example 1] By the suspension-polymerization method, the vinylidene-chloride system resin particle which consists of 50 % of the weight of vinylidene chlorides, 23 % of the weight of styrene, 20 % of the weight of acrylonitrile, 6.93 % of the weight of N-phenyl maleimide, and 0.07 % of the weight of 1,6-hexanediol diacrylate and which carried out partial bridge formation was obtained. Sinking-in processing was performed for HCFC142b at 60 degrees C to this particle for 24 hours. The content of obtained HCFC142b in a fizz vinylidene-chloride system resin particle was 10.3 % of the weight.

[0019] The raw material particle which mixed 2 weight sections for the magnesium carbonate was supplied to the raw material hopper of the simple foaming equipment illustrated to drawing 1 to this fizz vinylidene-chloride system resin particle 100 weight section, and the hot blast temperature in the foaming section was beforehand supplied continuously at the rate of 80 (a part for g/) on the screw in the foaming tub adjusted to 150 degrees C. The hot blast rate in the foaming tub upper part at this time was 350 (a part for m/).

[0020] From the exhaust port, the foaming particle it is 31 times whose expansion ratio of this was discharged by 80 (a part for g/). The foaming particle was not contracted but the interior of a particle had become multi-foam quality structure. Moreover, the amount of HCFC142b in a foaming particle is 10.0%, and is almost the same as the content in the particle before foaming, and the vaporization of the foaming agent at the time of foaming was not seen.

[0021]

[Example 2] The foaming particle was obtained like the example 1 except making hot blast temperature in the foaming section into 180 degrees C. The elimination rate of the foaming particle from an exhaust port was 80 (a part for g/), and it was 45 times the expansion ratio of this. The foaming particle was not contracted but the interior of a particle had become multi-foam quality structure. Moreover, the amount of HCFC142b in a foaming particle is 9.8%, and is almost the same as the content in the particle before foaming, and the vaporization of the foaming agent at the time of foaming was not seen.

[0022]

[Example 3] 60 degrees C sank into the pentane the vinylidene-chloride system resin particle which was obtained by the approach of an example 1 and which carried out partial bridge formation for 24 hours. The content of the pentane in the obtained vinylidene-chloride system resin fizz particle was 9.5 % of the weight. This vinylidene-chloride system resin fizz particle was made to foam by the same approach as an example 2.

[0023] The elimination rate of the foaming particle from an exhaust port was 80 (a part for g/), and it was 41 times the expansion ratio of this. The foaming particle was not contracted but the interior of a particle had become multi-foam quality structure. Moreover, the amount of pentanes

in a foaming particle is 9.4%, and is almost the same as the content in the particle before foaming, and the vaporization of the foaming agent at the time of foaming was not seen.

[0024]

[The example 1 of a comparison] The foaming particle was obtained like the example 1 except using the expandable polystyrene resin which contains butane 5.9% as a fizz resin particle. The elimination rate of the foaming particle from an exhaust port was as small as 30 (a part for g/), the foaming particle was contracted and expansion ratio was as small as 8 times. Moreover, the amount of butane in a foaming particle is 1.2%, and the foaming agent had vaporized at the time of foaming.

[0025]

[The example 2 of a comparison] The foaming particle was obtained like the example 2 except using the expandable polystyrene resin which contains butane 5.9% as a fizz resin particle. The elimination rate of the foaming particle from an exhaust port was as small as 20 (a part for g/), the foaming particle was contracted and expansion ratio was as small as 5 times. Moreover, the amount of butane in a foaming agent is 0.7%, and the foaming agent had vaporized at the time of foaming.

[0026]

[The example 3 of a comparison] As a fizz resin particle, the vinylidene-chloride system copolymer was used as the outer core, and the foaming particle was obtained like the example 1 except using endocyst and the fizz vinylidene-chloride system resin (the trade name of EXPANCEL-461DU, product made from Japanese FIRAITO, Inc.) currently encapsulated for butane 8.9%.

[0027] The elimination rate of the foaming particle from an exhaust port was as small as 20 (a part for g/), the foaming particle was contracted and expansion ratio was as small as 9 times.

[0028]

[Effect of the Invention] According to this invention, a foaming particle can be easily manufactured at spots for which the foaming particle of the high expansion ratio in a short time is needed, such as a civil work, with the simple equipment which makes hot blast by the electric-type hot blast generating machine the source of heating.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] In order to attain the manufacture approach of this invention, it is the mimetic diagram which illustrates effective equipment.

[Description of Notations]

- 1 Electric-Type Hot Blast Generating Machine
- 2 Heat-resistant Hose (50MmPhi, 1500MmL)
- 3 Thermometric Element
- 4 Temperature Element

- 5 Screen (200 Meshes)
- 6 Foaming Tub (20L.)
- 7 Raw Material Hopper (1L.)
- 8 Rotation Driving Source
- 9 Screw
- 10 Exhaust Port

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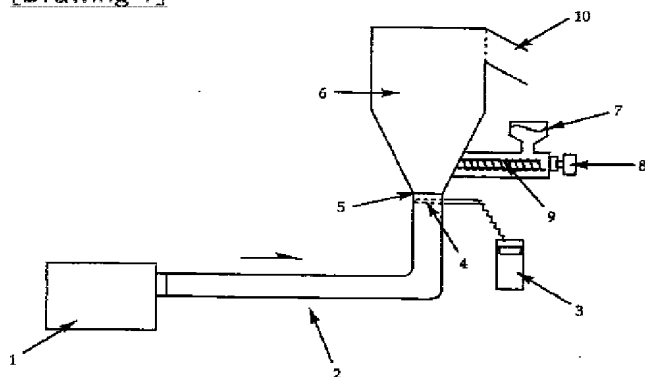
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DRAWINGS

[Drawing 1]



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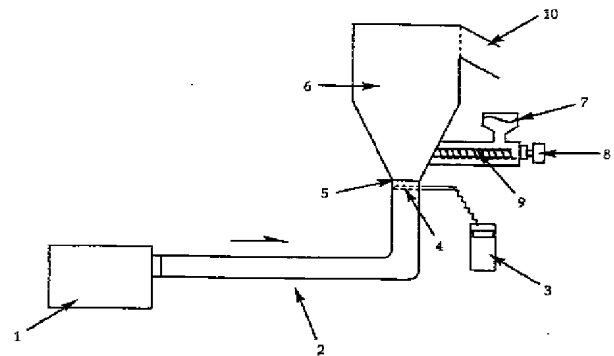
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(54)【発明の名称】 塩化ビニリデン系樹脂発泡性粒子の発泡方法及びその装置

(57)【要約】

【目的】 簡易な装置により、短時間で高発泡倍率の発泡粒子が必要とされる、土木工事等の現場で、容易に発泡粒子を製造する。

【構成】 部分架橋構造を有する塩化ビニリデン系樹脂発泡性粒子を電気式熱風発生機による熱風で発泡する方法であって、発泡槽における熱風の温度が100℃以上300℃以下、滞留時間が0.1分以上60分以下で発泡させる発泡粒子が安定化された多泡質構造となることを特徴とする発泡方法である。





## 【特許請求の範囲】

【請求項 1】 部分架橋構造を有する塩化ビニリデン系樹脂発泡性粒子を電気式熱風発生機による熱風で発泡する方法であって、発泡槽における熱風の温度が 100℃以上 300℃以下、滞留時間が 0.1 分以上 60 分以下で発泡させる発泡粒子が安定化された多泡質構造となることを特徴とする発泡方法。

【請求項 2】 100℃以上 300℃以下の熱風を発生する熱風発生機、該熱風を供給する耐熱性ホース、原料供給部および発泡粒子排出部を持つ発泡槽より構成される塩化ビニリデン系樹脂発泡性粒子を発泡させる装置。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、電気式熱風発生機による熱風を加熱源とする発泡性塩化ビニリデン系樹脂粒子の発泡方法に関するものであり、さらに詳しくは、簡易な装置により、短時間で高発泡倍率の発泡粒子が必要とされる、土木工事等の現地で、容易に発泡粒子を製造する方法、及びその装置に関する。

## 【0002】

【従来の技術】従来、発泡粒子が必要とされる現地での発泡性樹脂粒子の発泡方法としては、特公昭 35-11780 号公報や特公昭 38-16776 号公報に記載されている様に、ポリスチレン系樹脂粒子で蒸気を加熱源とする方法が知られている。しかし、ポリスチレン系樹脂はガスバリアー性に乏しいため、フォームハンドブック（日刊工業新聞社発行、昭和 48 年 2 月 28 日初版）の第 2 章に記載されている様に、発泡性ポリスチレン系樹脂は、水蒸気や熱風での加熱時間を長くしすぎると、発泡剤の粒子外部への揮散により、発泡粒子の収縮が起こり、逆に発泡倍率が低下する現象が生じ、発泡倍率の制御が困難である。

【0003】実際には、ポリスチレン系樹脂の発泡倍率を低下させないためには、発泡ガスの空気との置換をしたりするため、現場発泡では装置が大がかりとなり、操作も複雑になる。また、蒸気を加熱源とする限り、蒸気発生等の設備が必要であり、そのため装置は大型化し、発泡粒子が必要とされる現地への装置搬入には、大型トラック等が必要となり、例えば土木工事現場等では実用化されていない。

## 【0004】

【発明が解決しようとする課題】本発明の目的は、電気式熱風発生機による熱風を加熱源とする簡易な装置により、発泡粒子が必要とされる土木工事等の現地で、短時間で高発泡倍率の発泡粒子を製造方法、及びその製造方法に有効な製造装置を提供することである。

## 【0005】

【課題を解決するための手段】本発明は、部分架橋構造を有する塩化ビニリデン系樹脂発泡性粒子を電気式熱風発生機による熱風で発泡する方法であって、発泡槽にお

ける熱風の温度が 100℃以上 300℃以下、滞留時間が 0.1 分以上 60 分以下で発泡させる発泡粒子が安定化された多泡質構造となることを特徴とする発泡方法である。

【0006】また、本発明は、100℃以上 300℃以下の熱風を発生する熱風発生機、該熱風を供給する耐熱性ホース、原料供給部および発泡粒子排出部を持つ発泡槽より構成される塩化ビニリデン系樹脂発泡性粒子を発泡させる装置である。本発明は、発泡性樹脂粒子として、発泡粒子が安定化した多泡質構造となる、塩化ビニリデン系樹脂発泡性粒子を使用することにより達成できる。

【0007】塩化ビニリデン系樹脂は、ガスバリアー性に優れた樹脂である。従って、発泡時に粒子内部の発泡剤が揮散するのが少なく、発泡性樹脂粒子として発泡性ポリスチレン系樹脂粒子を使用した場合に見られる様に、発泡剤が急激に揮散することがないので、加熱時間を長期化しても発泡粒子の収縮は起こらないで、発泡粒子を安定化した多泡質構造とすることできる。このため電気式熱風発生機による熱風を加熱源とする簡単な装置で、発泡粒子が必要とされる土木現場等の現地で、短時間で高発泡倍率の発泡粒子を製造することが可能である。

【0008】と言うのも、電気式熱風発生機は熱風の温度、風量を調整することが比較的容易であり、かつ塩化ビニリデン系樹脂は、発泡時に粒子内部の発泡剤が揮散するのが少なく、簡易装置でも発泡の調整が容易である。本発明に使用される発泡性塩化ビニリデン系樹脂粒子は、特開昭 63-122745 号公報、特開昭 63-122713 号公報、特開平 04-085343 号公報等に記載されている。

【0009】すなわち、部分架橋した非晶質の塩化ビニリデン系樹脂粒子に、発泡剤を樹脂層全体に均一に含浸したものである。非晶質の塩化ビニリデン系樹脂粒子は、10 重量%以上、85 重量%以下の塩化ビニリデンを、15 重量%以上、90 重量%以下の一種類以上の塩化ビニリデンと共重合可能な単量体と、共重合することにより得ることができる。塩化ビニリデンの含有量が 10 重量%未満であるとガスバリアー性が低下し、発泡時の発泡剤の揮散が防止できない。一方、85 重量%を超えると、樹脂が結晶性となり、発泡剤の含浸が困難になる。

【0010】塩化ビニリデンと共重合可能な単量体としては、（メタ）アクリロニロニトリル、スチレン及びその誘導体、（メタ）アクリル酸メチル等の（メタ）アクリル酸エステル、N-フェニルマレイミド等の N-置換マレイミド類等を挙げることができる。さらに、部分架橋することで、多泡質構造の安定性が高まる。部分架橋を導入するためには、ジビニルベンゼンや脂肪族多価アルコールのメタアクリル酸エステル等の共重合性二重結

合を分子内に2個有する単量体を適当量共重合させれば良い。

【0011】該塩化ビニリデン系樹脂粒子の重合方法は、懸濁重合法、乳化重合法、溶液重合法等の公知の重合方法が使用できるが、重合体を粒子状で得ることのできる懸濁重合法が好ましい。粒子径としては、0.1mm以上5.0mm以下であることが好ましい。0.1mm未満では粒子の流動性が悪くなり、取扱い上好ましくなく、5.0mmを超えると発泡剤の含浸性が低下する。

【0012】本発明の目的を達成するためには、発泡性塩化ビニリデン樹脂粒子が発泡時に安定化された多泡質構造となることが必要である。多泡質構造とするためには、発泡剤を樹脂層全体に均一に含浸することが必要である。発泡剤を内包、カプセル化したものでは、発泡時に単一気泡となるために収縮しやすくなり、ある一定の狭い条件下でしか発泡させることができない。多泡質構造となることではじめて、幅広い条件下での発泡が可能となる。同じ、発泡性塩化ビニリデン系樹脂粒子であっても、塩化ビニリデン-アクリロニトリル等の熱可塑性樹脂を外核とし、発泡剤を内包、カプセル化した発泡性粒子（例えば、EXPANCELの商品名、日本フィライト株式会社製）は、発泡時に発泡粒子が単一気泡となるため、一定の条件下でしか発泡することができない。

【0013】塩化ビニリデン系樹脂粒子に、発泡剤を樹脂層全体に均一に含浸するための方法としては、該樹脂粒子と発泡剤を気体状や液体状で直接接触させる直接含浸法、樹脂粒子の水スラリーに発泡剤を添加する水中懸濁法、重合時に発泡剤を共存させておく重合含浸法等を使用することができる。発泡剤が樹脂層全体に均一に含浸されていることを確認するためには、樹脂粒子中の発泡剤の分布を赤外分光光度計や元素分析法等により調べることができる。

【0014】発泡剤としては、例えば、プロパン、ブタン、ペンタン、シクロペンタン等の炭化水素類；塩化メチル、塩化エチル等のハロゲン化炭化水素類；モノクロロジフルオロエタン（HCFCl<sub>4</sub>2b）等のHCFCl類；1,1,1,2-テトラフルオロエタン（HFC134a）等のHFC類等を使用することができる。本発明において、熱風温度は100℃以上300℃以下が好ましい。熱風温度が100℃未満の時は、発泡倍率が十分ではなく、300℃を超える時は、発泡樹脂粒子が熱分解する。

【0015】また、本発明において、熱風に暴露される樹脂粒子の滞留時間は、0.1分以上60分以下が好ましい。滞留時間が0.1分未満の時は、発泡倍率が十分ではなく、60分を超える時は、発泡粒子が熱分解する。本発明においては、未発泡塩化ビニリデン系樹脂粒子を直接発泡させても良いし、あらかじめ発泡させた予備発泡塩化ビニリデン系樹脂粒子をさらに発泡させても良

い。

【0016】図1は、本発明の製造方法の達成に有効な、簡易発泡装置を例示する模式図である。電気式熱風発生機（1）は、例えばTSK-10型熱風発生機の商品名（株式会社竹綱製作所製）で市販されている。発生した熱風は、耐熱性ホース（2）を通して、発泡槽（6）に送風される。温度検出器（3）で、発泡槽内に送風される熱風温度を測定し、熱風温度が所定の温度になる様に、熱風発生機の温度調節計を調整する。（7）の原料ホッパーを通し、スクリュウ（9）で発泡性塩化ビニリデン系樹脂粒子を発泡槽内に供給し、熱風により発泡させる。比重の小さくなった発泡粒子は、熱風により、排出口（10）より排出される。排出される発泡粒子の発泡倍率の調整は、発泡槽上部における熱風速度により行う。すなわち、熱風速度を上げると発泡倍率は小さくなり、熱風速度を下げると発泡倍率は大きくなる。

【0017】発泡剤が可燃性ガスの場合、引火する可能性があるため、発泡槽内の熱風が熱風発生機に逆流を防止する措置をとるとか、熱風の送風量と排出量を調節することで爆発限界外で操作することが必要である。その点塩化ビニリデン系樹脂は、ガスバリア性に優れるので、爆発限界外を選ぶ範囲は広い。また、熱風槽内の粒子同士の融着を防止するために、無機、有機の粉体等を粒子表面に介在させることができる。

【0018】

【実施例1】懸濁重合法により、塩化ビニリデン50重量%、スチレン23重量%、アクリロニトリル20重量%、N-フェニルマレイミド6.93重量%、1,6-ヘキサジオールジアクリレート0.07重量%からなる、部分架橋した塩化ビニリデン系樹脂粒子を得た。この粒子に対して、HCFCl<sub>4</sub>2bを60℃にて24時間、含浸処理を行った。得られた、発泡性塩化ビニリデン系樹脂粒子中のHCFCl<sub>4</sub>2bの含有量は、10.3重量%であった。

【0019】この発泡性塩化ビニリデン系樹脂粒子100重量部に対し、炭酸マグネシウムを2重量部を混合した原料粒子を、図1に例示した簡易発泡装置の原料ホッパーに投入し、スクリュウにより、80（g/分）の速度で、あらかじめ、発泡部における熱風温度を150℃に調整しておいた発泡槽内に、連続的に供給した。この時の発泡槽上部における熱風速度は、350（m/分）であった。

【0020】排出口から、発泡倍率が31倍の発泡粒子が、80（g/分）で排出された。発泡粒子は、収縮しておらず、粒子内部は多泡質構造となっていた。また、発泡粒子中のHCFCl<sub>4</sub>2b量は、10.0%であり、発泡前の粒子中の含有量とほぼ同じであり、発泡時の発泡剤の揮散は見られなかった。

【0021】

【実施例2】発泡部における熱風温度を180℃とする

以外は、実施例 1 と同様にして、発泡粒子を得た。排出口からの発泡粒子の排出速度は、80 (g/分) であり、発泡倍率は 45 倍であった。発泡粒子は、収縮しておらず、粒子内部は多泡質構造となっていた。また、発泡粒子中の HCFC 142b 量は、9.8% であり、発泡前の粒子中の含有量とほぼ同じであり、発泡時の発泡剤の揮散は見られなかった。

【0022】

【実施例 3】実施例 1 の方法で得られた部分架橋した塩化ビニリデン系樹脂粒子をペンタンに 60℃、24 時間含浸した。得られた塩化ビニリデン系樹脂発泡性粒子中のペンタンの含有量は、9.5 重量% であった。この塩化ビニリデン系樹脂発泡性粒子を、実施例 2 と同様の方法で発泡させた。

【0023】排出口からの発泡粒子の排出速度は、80 (g/分) であり、発泡倍率は 41 倍であった。発泡粒子は、収縮しておらず、粒子内部は多泡質構造となっていた。また、発泡粒子中のペンタン量は、9.4% であり、発泡前の粒子中の含有量とほぼ同じであり、発泡時の発泡剤の揮散は見られなかった。

【0024】

【比較例 1】発泡性樹脂粒子として、ブタンを 5.9% 含有している発泡性ポリスチレン樹脂を使用する以外は、実施例 1 と同様にして、発泡粒子を得た。排出口からの発泡粒子の排出速度は、30 (g/分) と小さく、発泡粒子は収縮しており、発泡倍率は 8 倍と小さかった。また、発泡粒子中のブタン量は、1.2% であり、発泡時に発泡剤が揮散していた。

【0025】

【比較例 2】発泡性樹脂粒子として、ブタンを 5.9% 含有している発泡性ポリスチレン樹脂を使用する以外は、実施例 2 と同様にして、発泡粒子を得た。排出口からの発泡粒子の排出速度は、20 (g/分) と小さく、\*

\* 発泡粒子は収縮しており、発泡倍率は 5 倍と小さかった。また、発泡剤中のブタン量は、0.7% であり、発泡時に発泡剤が揮散していた。

【0026】

【比較例 3】発泡性樹脂粒子として、塩化ビニリデン系共重合体を外核とし、ブタンを 8.9% 内包、カプセル化している、発泡性塩化ビニリデン系樹脂 (EXPANCEL-461DU の商品名、日本ファイナ株式会社製) を使用する以外は、実施例 1 と同様にして、発泡粒子を得た。

【0027】排出口からの発泡粒子の排出速度は、20 (g/分) と小さく、発泡粒子は収縮しており、発泡倍率は 9 倍と小さかった。

【0028】

【発明の効果】本発明によれば、電気式熱風発生機による熱風を加熱源とする簡易な装置により、短時間で高発泡倍率の発泡粒子が必要とされる、土木工事等の現地で、容易に発泡粒子を製造することができる。

【図面の簡単な説明】

【図 1】本発明の製造方法を達成するために、有効な装置を例示する模式図である。

【符号の説明】

- 1 電気式熱風発生機
- 2 耐熱性ホース (50mmφ, 1500mmL)
- 3 温度検出器
- 4 温度検出端
- 5 スクリーン (200メッシュ)
- 6 発泡槽 (20リットル)
- 7 原料ホッパー (1リットル)
- 8 回転駆動源
- 9 スクリュー
- 10 排出口

【図 1】

